

EFFECT OF CARRIER GAS ON TAR YIELD AND
QUALITY OF OCCIDENTAL FLASH PYROLYSIS

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ABSTRACT

Occidental Flash Pyrolysis employs recycled heated char as heat carrier to supply the heat of pyrolysis. When nitrogen was used, as transport gas, tar yield decreased due to char-catalyzed tar cracking reactions. When low surface area heat carrier was used, tar cracking reactions was prevented and the tar yield was raised back to the expected level.

The tar was lighter with lower average molecular weight. The improvement of tar yield and quality was attributed to the stabilization of reactive coal fragments by nascent hydrogen produced by char gasification (by CO₂ and steam) and water-gas shift reactions.

INTRODUCTION

Flash Pyrolysis of coal employs very rapid heating to devolatilize pulverized coal in the absence of air to partition the coal into hydrogen-rich tar and carbon-rich char residue. It has been studied in both batch and continuous reactors. (1-5)

Occidental Research Corporation (ORC) developed this concept in a novel entrained flow reactor in which hot recycled char provides the heat to pyrolyze the coal. The typical tar yields are approximately twice that obtained from Fischer Assay test from the same coal. The detailed description of ORC process has been provided elsewhere.(6)

During the operation of a 3-ton-per-day process development unit (PDU), tar loss by char-catalyzed tar cracking reactions was uncovered. A smaller scale unit, 1 kg-per-hour bench scale reactor (BSR), was used to study the effects of transport gas and heat carrier on tar yield. Reactive gases such as CO₂ and H₂O instead of nitrogen were used to transport the char. Tar loss was prevented when the high surface area of char was covered by reactive gases. The tar yield was increased to the same level as that predicted by the electrical heating cases. When low surface area aluminum was used as heat carrier tar loss was also prevented. These results and the mechanism to prevent the tar loss were discussed by Duraiswamy et.al. (7)

This paper presents the effect of carrier gas and heat carrier on the tar quality.

EXPERIMENTAL

The experiments for pyrolysis of coal were carried out in a 1 kg-per-hour bench scale reactor as shown in Figure 1. Coal was metered by a screw feeder and carried by transport gas into the reactor. Char was metered by a second screw feeder and carried by nitrogen or desired transport gas. The char was preheated to the desired temperature before it mixed with the coal. Coal particles were brought to the pyrolysis reaction temperature in a few milliseconds.

Coal disproportionated into hydrogen-rich volatiles and carbon-rich char. The char was separated in a series of cyclones and the vapors and gases were cooled to collect the liquid products. The effluent gases were analyzed by gas chromatographs. The condensed liquid product is dissolved in acetone for easy removal from the collection vessels. After evaporation of the acetone under vacuum, tar and water are separated by distillation.

Each of the fractions, namely acetone, water and tar, are analyzed separately to determine water, light oil and tar ($110^{\circ}\text{C}+$). Tar in condensed water, tar left in char, if any, as determined by pyridine solubility and tar adsorbed in the activated charcoal, as determined by Fischer Assay are all included in the total tar yield.

For the purpose of this study, the characterization of tar properties was only carried out on the $110^{\circ}\text{C}+$ fraction material which is usually over 90% of the "tar".

The analyses of coal and char are given in Table 1. The molecular weight distribution profiles were determined by using gel permeation chromatography performed on tar samples using a Waters 244 ALC/GPC Liquid Chromatograph equipped with a refractive index detector. The columns employed were Waters styragel-columns 30 cm x 7.8 mm ID consisting of 1-1000A, 1-500A and 3-100A pore size packings. Tetrahydrofuran, THF from Burdick and Jackson, was used as the solvent at a pressure of 1000 psig. Calibration of the instrument used the polystyrene standards ranging in molecular weight from 100 to 33,000 AMU. Therefore, the molecular weight labeling of GPC chromatograms was for reference and comparison purpose.

GPC samples were prepared by adding 8 drops of 15% solution of tar in THF to 5 ml THF and filtering through a 0.65 micron filter sample sizes were 125 μl .

The tar was subjected to a solvent fractionation procedure to yield oils, asphaltenes and preasphaltenes. The solubility classes were defined as: oils (hexane soluble), asphaltenes (hexane insoluble/toluene soluble) and preasphaltenes (toluene insoluble/pyridine soluble). Separation was obtained according to the procedure described in Ref. (6).

RESULTS AND DISCUSSIONS

For the purpose of this study, the initial pyrolysis experiments were performed using subbituminous coal, nitrogen carrier gas and electrical heating; i.e., no preheated char was used. A series of runs ranging from 1000°F to 1400°F was carried out. The yields and properties of tar for these runs are given in Table 2.

Effect of Residence Time

Tar produced at the longer residence time contained a higher proportion of oil, and was also characterized by a lower specific gravity, lower viscosity and lower sulfur content than that produced at the lower residence time. These improved tar properties were attributed to the additional cracking that occurs at the longer residence time.

The evidence of the additional tar cracking due to longer residence time is provided by GPC chromatograms, Figure 2. They show that at longer residence times, the concentrations of high molecular weight species decreased while the concentrations of lower molecular species increased.

The oil content of tar was relatively independent of the pyrolysis temperature but was affected by the residence time as shown in Figure 3. The oil content increased from an average value of 43% to 54% when the residence time increased from 1.5 to 3 seconds with a corresponding decrease in the preasphaltenes content. The data suggested that asphaltenes and preasphaltenes underwent cracking at longer residence times and thus the proportion of oil increased. These results indicate that chemical transformations of the tar which occurred during the process enhanced its properties without suffering significant loss in yields. More importantly, these reactions apparently occurred over a practical and controllable range of residence times.

Effect of Heat Carrier: Char and Alumina

When preheated char was used as heat carrier, the tar yields decreased as the ratio of char-to-coal increased, as shown in Figure 4. This effect has been attributed to the char-catalyzed tar cracking reaction by DuraiSwamy et. al.⁽⁷⁾ Due to the secondary cracking reactions, the tar is lighter compared to the tar produced in the electrical heating mode as shown in Table 3. The higher atomic hydrogen-to-carbon ratio and oil content were indications of tar cracking.

When the low surface area (0.23 m²/g) alumina was used as heat carrier, the tar yield was higher than the case which used char as heat carrier. The tar is lightest among the three as shown in GPC of Figure 5. The tar loss reaction by char-catalyzed cracking was prevented when alumina was used as heat carrier. However, a different catalytic reaction might have taken place on the surface of alumina to improve the tar quality, as shown by the GPC.

GPC of tar from the alumina run showed significant reduction of heavy species. This could be attributed to a second possibility that the tar could not lay down on the surface of heat carrier polymerization or condensation to form heavy tar was prevented. The effect on tar yield and quality can be summarized in the following:

Tar Yield: Electrical > Alumina > Char

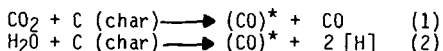
Tar Quality: Alumina > Char > Electrical

Petroleum fluid coke was used in PDU tests instead of alumina and it was found to be in between alumina and char for improving the tar yield and quality.

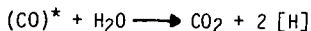
Effect of Reactive Carrier Gases

When different kinds of carrier gases such as CO, CO₂ and steam were used, the tar produced were lighter. The properties are summarized in Table 4. The molecular weights of tars were reduced as shown by vapor phase osmometric analysis and GPC profiles of Figure 6. The high polymeric species such as asphaltenes and preasphaltenes also decreased.

The tar yields were as high as the electrical heating case. The improvement of tar yield and quality were due to the adsorption of reactive gases on the char. When the surface area of char is occupied, tar vapor will not get adsorbed and get cracked on the surface of char to form coke and gases. Additionally by CO₂ and steam char gasification takes place producing CO and [H].



Where (CO)* is surface adsorbed carbon oxides. Nascent hydrogen can be formed on the surface of char by water-gas-shift reaction.



When the primary pyrolysis fragments (free radicals) are formed, they are seeking for stabilization by either reacting with the nascent hydrogen in the gas phase or on the char surface or recombining (polymerizing) stabilization of reactive fragments by nascent hydrogen prevents polymerization reaction to form heavy molecular weight species and coke.

CONCLUSION

Both carrier gas and heat carrier were found to affect the tar yield and tar quality in the Flash Pyrolysis of coal. Preheated char of high surface area provided adsorption sites for tar vapor. Tar either polymerized or cracked on the char to form gases and coke thus lowering the tar yield. When low surface area heat carrier were used, tar loss was reduced significantly. When the active sites of preheated char were occupied by reactive gases such as CO₂ and tar loss was prevented, and the tar quality was also improved. This improvement was attributed to the stabilization of pyrolysis free radicals by the nascent hydrogen produced from carbon gasification between char and reactive gases.

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TABLE 1
ANALYSES OF FEED COAL AND CHAR

	<u>Feed Coal</u>	<u>Feed Char</u>	<u>Product Char</u>
<u>Proximate Analysis, Wt.%</u>			
Moisture	11.59	1.18	0.7
Ash	5.00	11.40	10.00
Volatile Matter	37.01	7.02	7.88
Fixed Carbon	46.40	80.40	81.42
<u>Ultimate Analysis (Dry), Wt.%</u>			
Carbon	69.12	82.27	82.63
Hydrogen	4.95	1.87	2.13
Oxygen	18.32	2.52	3.29
Nitrogen	1.29	1.14	1.11
Sulfur	0.66	0.66	0.57
Ash	5.66	11.54	10.27
<u>Fischer Assay, Wt.%</u>			
Char	60.4	-	-
Water	21.4	-	-
Tar	9.3	-	-
Gas	8.9	-	-

Table 2
YIELDS AND PROPERTIES OF SUBBITUMINOUS COAL TAR

Pyrolysis Conditions

Residence time, seconds	1.5	3.0
Run Number	132 130 134	135 133 131
Temperature, °F	1000 1200 1400	1000 1200 1400
Tar Yield, wt % MAF	8.7 17.3 15.2	15.2 14.7 9.7

Tar Properties

I. Physical Data:					
Specific Gravity, (80/80°F)	1.170	1.171	1.250	1.097	1.090
Viscosity, Centipoises (@ 415°F and extrapolated to)	45	54	23	16	12
0 sec-1 shear)					
Melting Point, °F	230-265	194-230	-	-	68
					86-104

II. Ultimate Analysis, wt% (Dry Basis)

Ash	0.7	0.15	0.05	0.02	0.04	0.08
Carbon	79.34	80.41	80.86	79.41	79.46	85.49
Hydrogen	7.44	7.47	6.35	7.75	6.73	5.82
Sulfur	0.51	0.65	0.49	0.39	0.51	0.71
Nitrogen	1.25	1.42	1.45	1.04	1.41	1.80
Oxygen (by difference)	11.39	9.90	10.80	11.39	11.85	6.10
Atomic H/C	1.13	1.11	0.95	1.17	1.02	0.82

III. Solubility Classification, wt%

Oil	43	42	44	56	53	55
Asphaltenes	29	30	28	27	30	21
Preasphaltenes	28	28	28	16	17	24

TABLE 3
COMPARISON OF TAR PROPERTIES
EFFECT OF CHAR HEAT CARRIER

Run No.	<u>175</u>	<u>139</u>	<u>141</u>
Carrier Gas	N ₂	N ₂	N ₂
Preheater Temp °F	----	1200	1200
Pyrolysis Temp. °F	1200	1255	1255
Residence Time, Sec.	2.0	1.2	1.5
Char/Coal Ratio	0 (electric)	3.3	5 (Alumina)
Tar Yield (wt.%)MAF	18.0	9.7	14.1
Sp. Gravity, 60/60°F			
g/cc	1.218	1.191	-
Ultimate Analysis %Wt.			
C	81.47	80.00	76.81
H	6.32	6.68	6.75
N	1.14	1.48	1.12
S	0.55	0.43	0.38
O	10.52	11.40	14.94
Atomic H/C	0.93	1.00	1.05
VPO MW	285	--	--
Solubility Classification, Wt.%			
Pre-asphaltenes	25.6	17.1	--
Asphaltenes	33.0	24.6	--
Oil	41.4	58.3	--

TABLE 4
PROPERTIES OF TARS USING REACTIVE CARRIER GASES

BSR Run	176	177	178
Temperatures, °F char preheater	1500	1500	1500
Reactor	1191	1200	1200
Char/Coal Ratio	3	3	3.3
Carrier Gas	Steam (50%) CO (50%)	Steam (10%) CO ₂ (90%)	CO ₂
Residence Time, sec	1.9	1.94	2.0
Tar Yield, %MAF coal	15.2	19.2	18.3
Ultimate Analysis, % Wt			
C	80.78	81.22	80.15
H	6.25	6.48	6.34
N	1.47	1.43	1.58
S	0.66	0.56	0.61
O (by diff)	10.77	10.31	11.39
Ash	0.07	-	-
Atomic H/C	0.928	0.957	0.949
Sp. Gravity, 60/60°F			
g/cc	1.195	1.183	1.183
°API	-13.1	-11.9	-11.9
VPO MW	275	254	245
Solubility Classification, Wt%			
Preasphaltenes	16.9	16.3	17.4
Asphaltenes	28.6	28.4	27.2
Oil (by diff)	54.5	55.3	55.4

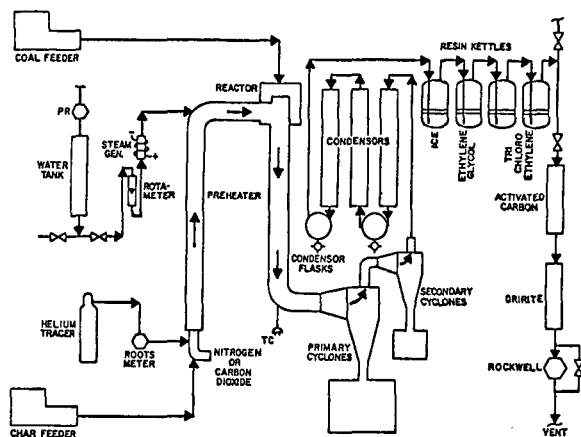


FIGURE 1 FLOW DIAGRAM OF 1 Kg-PER HOUR BENCH SCALE REACTOR

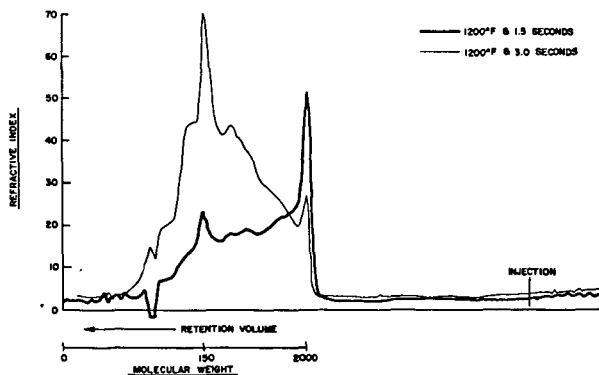
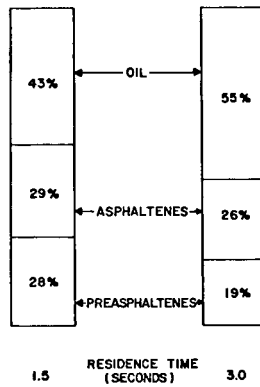


FIGURE 2 GEL PEMEATION CHROMATOGRAMS OF SUBBITUMINOUS COAL TARS PRODUCED AT 1200°F.



YIELDS, RELATIVELY TEMPERATURE INDEPENDENT,
WERE AVERAGED FROM RUNS AT 1000-1200-1400°F

FIGURE 3 SOLUBILITY CLASSIFICATION OF
SUBBITUMINOUS COAL TARS AS A
FUNCTION OF RESIDENCE TIME.

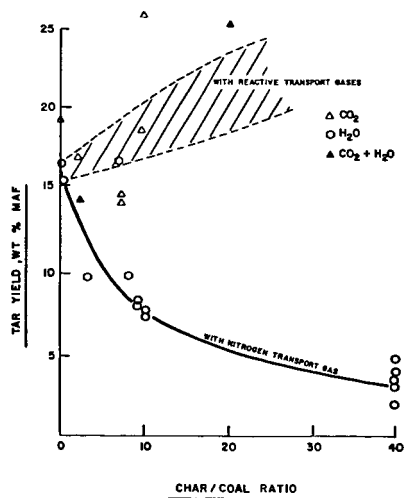


FIGURE 4 EFFECT OF RECYCLED CHAR ON
TAR YIELD

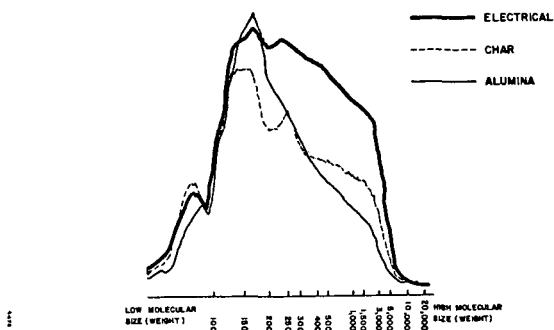


FIGURE 5 EFFECT OF SOLID HEAT CARRIER ON THE MOLECULAR SIZE DISTRIBUTION OF TARS.

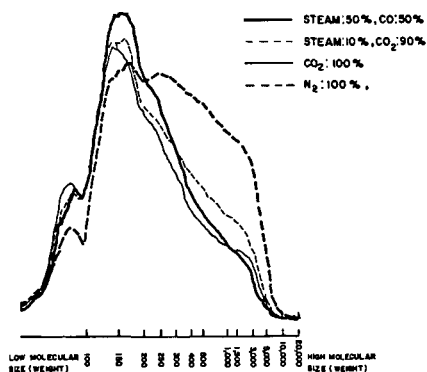


FIGURE 6 EFFECT OF CARRIER GASES ON THE MOLECULAR SIZE DISTRIBUTION OF TARS.

ISOTHERMAL FURNACE STUDIES OF THE KINETICS OF LIGNITE PYROLYSIS

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INTRODUCTION

In practical pulverized coal combustors and gasifiers, pyrolysis occurs in conjunction with rapid heating of the coal; heating rates in excess of $1,000^{\circ}\text{C/s}$ being common. One apparent consequence of rapid heating is that crucial reactions occur in the first few seconds or even milliseconds (1-3). This is partially responsible for the stringent requirements associated with an acceptable experimental technique for studying the kinetics of rapid coal pyrolysis. The requirements include controlled rapid heating, isothermal reaction, variation of reaction time and rapid quenching. In essence, it is essential to have unambiguous reaction history.

Two of the techniques currently in use more or less satisfy the requirements. One employs essentially monolayer samples heated on an electrical grid (1), and the other utilizes a flow of coal particles injected into a preheated gas stream (2,3). The latter technique is used in this laboratory. The kinetics of pyrolysis are most conveniently studied using an inert atmosphere as the pyrolyzing medium. This has the effect of decoupling pyrolysis reactions from other heterogeneous gas/solid reactions that occur when a reactive atmosphere such as H_2 is used. Present data are for isothermal pyrolysis in N_2 of a lignite from the Darco Seam in Texas. Temperatures vary from 700 to $1,000^{\circ}\text{C}$ and particle size fractions, from 60 x 80 to 270 to 400 mesh.

EXPERIMENTAL

Pyrolysis is performed in an entrained flow, isothermal furnace similar to that described by Nsakala and co-workers (3) which, in turn, is based on the design of Badzioch and Hawksley (4). It is, in essence, a vertical reactor heated electrically and for the injection of a dilute coal stream into the center of a preheated gas stream. The ensuing mixing heats the injected stream at a rate of about $10,000^{\circ}\text{C/s}$. The injector is designed to minimize migration and adherence of coal particles to the furnace tube wall. A water-cooled sampling probe, which is inserted up the axis of the furnace, collects and rapidly quenches the particle stream. The reactor tube is heated uniformly so that pyrolysis is essentially contained in an isothermal region. Variable positioning of the sampling probe adjusts the reaction time. A schematic of the equipment is shown in Figure 1 and the operating conditions are given in Table 1.

Weight loss due to pyrolysis is determined using proximate ash as a tracer. Data are corrected for the error associated with this technique. For the Darco lignite the error is less than 10% and is thought to result from the loss of sulfur during pyrolysis (5). The proximate analysis of the lignite is given in Table 2. Particle size fractions are separated by dry sieving and characterized by the Rosin-Rammler technique (6).

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TABLE 1. OPERATING CONDITIONS

	Gas and Wall Temperature, °C			
	700	800	900	1,000
Coal Feed Rate, g/min	1.0	1.0	1.0	1.0
Mean Gas Velocity, m/s	1.12	1.12	1.12	1.12
Secondary/Primary N ₂	16.7	15.0	13.7	12.5
Coal Loading, wt%	2.2	2.5	2.7	2.9
Gas Reynolds Number	458	391	339	298

TABLE 2. PROXIMATE ANALYSIS OF THE DARCO LIGNITE

	<u>as-received</u>	<u>dry</u>	<u>daf</u>
Moisture, %	22.4	-	-
Ash, %	12.4	15.9	-
Volatile Matter, %	33.3	43.0	50.2
Fixed Carbon, %	31.9	41.1	49.8

Equilibrium Moisture = 39.8%

RESULTS

A typical weight loss versus time curve is shown in Figure 2 for isothermal pyrolysis at 900°C. Weight loss, hence pyrolysis rate, is independent of particle size over the range 60 x 80 to 270 x 400 mesh. The corresponding range in mean particle size is 40 to 200 μ m. Similar curves are obtained at 700, 800 and 1,000°C.

The maximum potential weight loss in the isothermal furnace is not measurable by a single pass because of the restricted residence time. It is calculated by the method of Badzioch and Hawksley (4). This involves establishing a relationship between the change in proximate volatile matter between the original dry-ash-free coal and char and weight loss due to pyrolysis. The derived relationship is linear; it is essentially particle size (Figure 3) and temperature independent (Figure 4) for the range of operating conditions. The maximum weight loss is 66% of the daf coal, representing a fractional increase of 1.3 over the proximate volatile matter. The weight loss achieved by a single pass in the isothermal furnace at 1,000°C and a total residence time of 0.4 s is 50% of the daf coal, indicating about 80% completion of pyrolysis.

A first-order plot for pyrolysis at 900°C is shown in Figure 5. A feature of the curve is the apparent delay in the onset of pyrolysis during heat-up of the particles. This is in agreement with the findings of Jüntgen and Van Heek (7). Correlating first-order rate constants by the Arrhenius expression (Figure 6) yields a pseudo activation energy of 7.7 kcal/mole and a pre-exponential factor of 92 s^{-1} .

DISCUSSION

Successful description of the kinetics of pyrolysis up to 80% completion by a single first-order reaction equation is not inconsistent with the need for a second equation to describe the completion of pyrolysis as postulated by Nsakala and co-workers (3). This derives from the fact that the second component devolatilization is associated mainly with H_2 liberation (8), which on a weight basis accounts for only about 5% of the daf coal.

The relatively low pseudo activation energy is consistent with the data presented by Anthony and Howard (9). The absence of particle size effects on the rate of pyrolysis for the Darco lignite essentially implies the absence of significant heat and mass transfer effects. Since low activation energies are usually associated with these physical factors, an alternative explanation is required here. Howard and co-workers (1,9) provide a probable explanation in terms of a distribution of activation energies for the generation of different volatile species. They obtain an activation energy of about 10 kcal/mole in a single-step correlation and about 50 kcal/mole in a multistep model.

SUMMARY

The present work further demonstrates the suitability of the entrained flow isothermal furnace for studying the kinetics of lignite pyrolysis. Under rapid heating conditions there is a delay in the onset on significant pyrolysis during particle heat-up. For the Darco lignite, pyrolysis up to 80% completion follows a single first-order reaction equation; but a second equation may be necessary to describe the completion of pyrolysis. The relatively low activation energy of less than 10 kcal/mole and the absence of significant particle size effects are not necessarily inconsistent, as the former may not necessarily indicate physical rate control.

ACKNOWLEDGEMENTS

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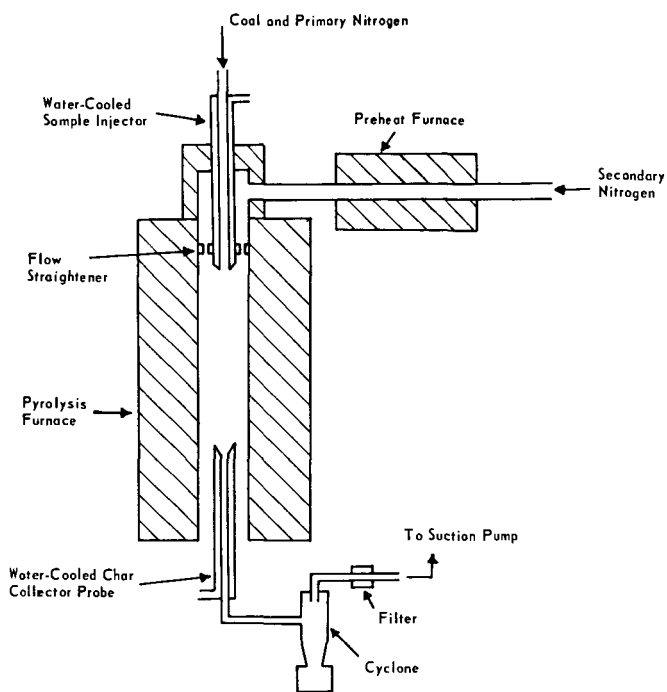


Figure 1. SCHEMATIC OF EQUIPMENT

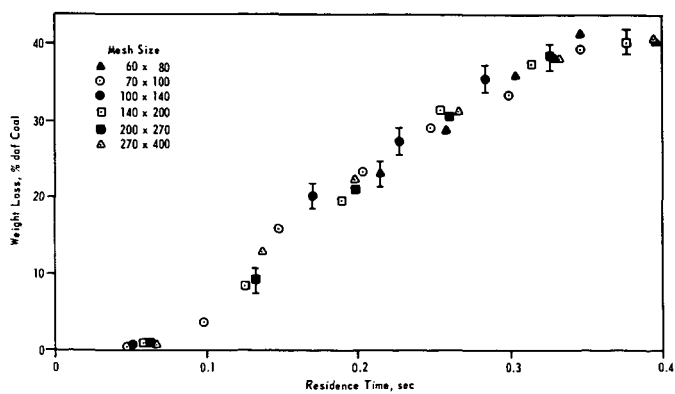


Figure 2. WEIGHT LOSS AS A FUNCTION OF RESIDENCE TIME OF LIGNITE IN REACTOR AT 900°C

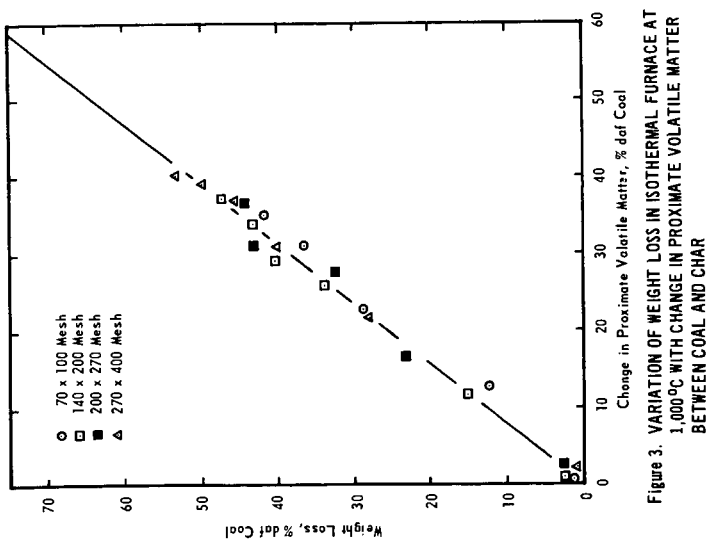


Figure 3. VARIATION OF WEIGHT LOSS IN ISOTHERMAL FURNACE AT 1,000°C WITH CHANGE IN PROXIMATE VOLATILE MATTER BETWEEN COAL AND CHAR

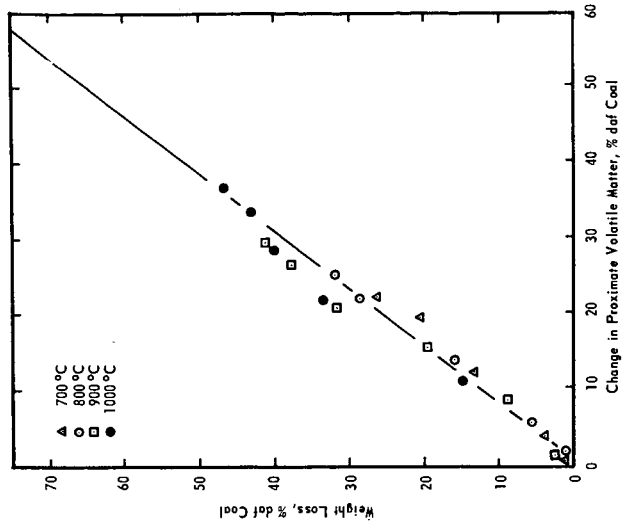


Figure 4. VARIATION OF WEIGHT LOSS IN ISOTHERMAL FURNACE WITH CHANGE IN PROXIMATE VOLATILE MATTER BETWEEN COAL AND CHAR FOR 140 x 200 MESH SIZE FRACTION

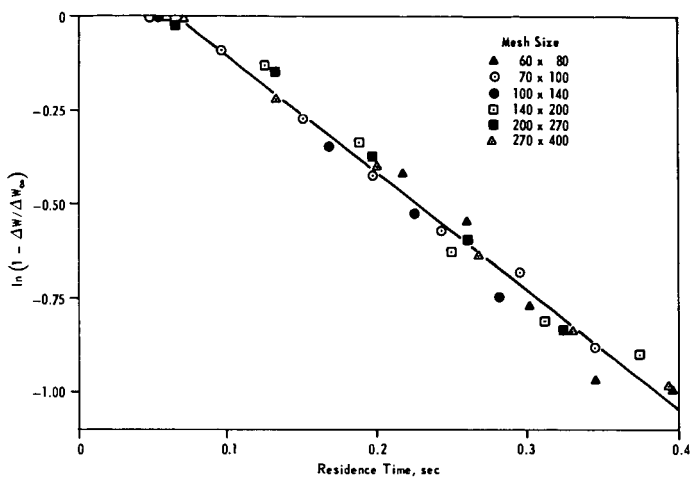


Figure 5. FIRST ORDER PLOT FOR DEVOLATILIZATION WEIGHT LOSS FOR LIGNITE AT 900°C

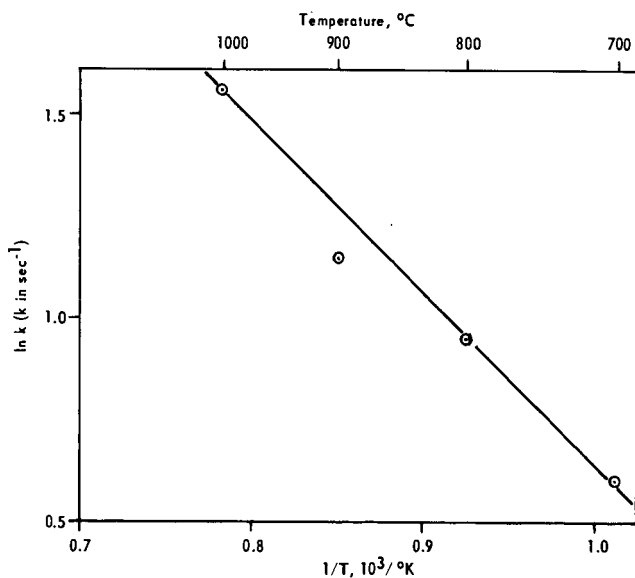


Figure 6. ARRHENIUS PLOT FOR LIGNITE DEVOLATILIZATION TREATED AS ONE STEP, FIRST-ORDER REACTION

RATES OF LIGHT GAS PRODUCTION BY DEVOLATILIZATION OF COALS AND LIGNITE

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INTRODUCTION

The kinetics of coal pyrolysis are important in many coal conversion processes which operate under conditions of relatively moderate temperatures (400° to 1000°C). Such processes range from in situ coal gasification (1) to flash hydropyrolysis (3), having anticipated coal residence times in the region of pyrolysis temperatures of between 10^{-1} and 10^4 seconds - a range of five orders of magnitude.

Although many models have been postulated for coal devolatilization (4), Howard and his co-workers (2,4) have shown that the use of a statistical distribution of activation energies can provide "valuable insight into the overall or global kinetics of the [pyrolysis] process," particularly with regard to explaining the effects of heating rate. They therefore state (4) that, "For a designer seeking a correlation of devolatilization yields, [the distributed activation energy model] combined with a description of secondary reactions is presently the best recommendation." Ciuryla et al. (6) have since shown that the parameters (mean activation energy, standard deviation of the energy distribution, and total potential volatilization) obtained by fitting total weight loss data obtained at heating rates of 40 and 160°C/min, for a Montana lignite and a Pittsburgh Seam bituminous coal, are close to the values reported by Anthony and Howard for the same coals at heating rates of 100 to 10,000°C/sec.

The distributed activation energy model has not previously been applied to data for the yields of individual molecular species from coal pyrolysis. It has normally been assumed (with good results for data obtained over a narrow range of heating rates) that the yields of individual species can be modelled by a small set of individual reactions representing the major mechanisms for their production. However, it has been recognized (2) that the parameters obtained from such models are only "effective" values which may have no fundamental significance. It can be shown (see below) that the values typically obtained from models having a small number of individual reactions cannot be applied over a wide range of heating rates.

EXPERIMENTAL

Coal Samples

The North Dakota lignite and Illinois No. 6 bituminous coal samples used in this study were provided by the Pennsylvania State University. The Pittsburgh Seam bituminous and Wyodak subbituminous coal samples were obtained from Commercial Testing and Engineering Company; these samples were ground under inert atmosphere. Proximate and ultimate analyses of the coals studied are given in Table 1. Sized, 40 x 80 mesh, samples were used in all runs.

Apparatus

The primary apparatus used in obtaining the results reported herein was a 6-gram-capacity thermobalance built specifically for Air Products' laboratories by Spectrum Products, Inc. This apparatus is essentially identical to equipment which was previously in existence at Case-Western Reserve University (5). The apparatus consists of a cylindrical basket, containing the coal sample, which is suspended from a balance arm into an externally heated Haynes 25 superalloy tube. Although the apparatus is capable of operation at pressures up to 1500 psi, only results obtained at atmospheric pressure, in helium, are reported here. Heating rates were monitored by thermocouples

on the tube wall, and also inside the tube near the basket, it having been determined (by placing a thermocouple in the basket itself) that the differences between the sample temperature and the wall temperature were small.

Experimental Procedure

Approximately 3 gms of dry, 40 x 80 mesh, coal were placed inside the sample basket and lowered into the reactor at room temperature. After purging the system with helium, the reactor was heated. The temperature, monitored by a thermocouple located immediately below the sample basket, the helium flow rate, and the sample weight were continuously recorded. Gas samples were periodically collected by syringes through a septum in the heated exit line. These samples were subsequently analyzed using a Perkin-Elmer Sigma-1 gas chromatograph.

The helium flow rate was maintained at approximately 700 cc/min. Due to the heat capacity of the tube and furnace, and to heat losses from the furnace, the heating rate was not constant during the experiments; however, the observed rates can be approximated by the formula

$$\frac{dT}{dt} = 10.8 - 0.00642 \cdot T$$

where T = sample temperature, $^{\circ}\text{C}$, and t = time, minutes. The actual recorded time/temperature data were used in the computer analysis of the results.

Kinetic Model

Coal pyrolysis has frequently been assumed to be described by a set of parallel first-order reactions (1,2,4). For each reaction, i , the corresponding devolatilization rate is

$$\frac{dV_i}{dt} = k_i e^{-\frac{E_i}{RT}} (V_i^* - V_i) \quad (1)$$

where k_i is the preexponential factor and E_i is the activation energy of reaction i ; V_i is the amount of volatile product produced by reaction i up to time t ; V_i^* is the amount of product which could potentially be produced; T is the absolute temperature, and R is the gas constant. The total yield from reaction i at time t is therefore

$$\frac{V_i^* - V_i}{V_i^*} = \exp \left\{ -k_i \int_0^t e^{-\frac{E_i}{RT}} dt \right\} \quad (2)$$

For the case of constant heating rate, $m = dT/dt$, it has been shown (2) that, since $E_i/RT \gg 1$ for coal pyrolysis reactions, the solution of Equation 2 is

$$\frac{V_i^* - V_i}{V_i^*} = \exp \left\{ -\frac{k_i RT^2}{m E_i} e^{-\frac{E_i}{RT}} \right\} \quad (3)$$

(This equation may be extended to include a holding period at pyrolysis temperature and/or the subsequent cool-down period, as shown in the Appendix.)

Integration of Equation 2 for the case of nonconstant heating rate may easily be done numerically; however, provided that

$$\frac{RT}{E_i} \cdot \frac{T}{m} \cdot \frac{dm}{dT} \ll 1$$

Equation 3 with $m = m(T)$ can be used.

The distributed activation energy model assumes that the activation energy for producing volatile material (or a specific volatile product) is normally distributed about a mean value, E_{i0} , with k_i constant. The result, analogous to Equation 3, is

$$\frac{V_i^* - V_i}{V_i^*} = \frac{1}{\sigma\sqrt{2\pi}} \int_0^{\infty} \exp \left[-\frac{k_i RT^2}{mE} \right] e^{-\frac{E}{RT}} \exp \left[-\frac{(E-E_{i0})^2}{2\sigma^2} \right] dE \quad 4)$$

where σ is the standard deviation of the energy distribution. (In practice, integration from $E = 1$ kcal/mol to $E = E_{i0} + 4\sigma$ is adequate for analyzing the data.)

The rate of devolatilization at temperature T is

$$\frac{1}{V_i^*} \frac{dV_i}{dt} = \frac{k_i}{\sigma\sqrt{2\pi}} \int_0^{\infty} e^{-\frac{E}{RT}} \exp \left[-\frac{k_i RT^2}{mE} \right] e^{-\frac{E}{RT}} \exp \left[-\frac{(E-E_{i0})^2}{2\sigma^2} \right] dE \quad 5)$$

RESULTS AND DISCUSSION

Figures 1 through 5 present the pyrolysis rate data, for each of the five coals, for the four major noncondensable products of pyrolysis (hydrogen, carbon monoxide, carbon dioxide, and methane). The total weight loss is also shown. The initial appearance of these species occurs in the same order for all of the coals: CO_2 appears first, followed by CO , CH_4 , and, finally, H_2 . However, the maximum rate of CO production does not occur until well after that of methane; the temperature of the maximum rate of CO production is nearly coincident with that of the maximum rate of hydrogen production (about 700°C). (The CO production rate is actually bimodal, with a small peak at about 450°C and a larger peak at about 700°C , for the low-rank coals.) The observed peaks for C_2 and C_3 hydrocarbons (not shown) occur at the same temperature as those for methane. The major differences among the coals are in the amounts of CO and CO_2 produced, which are, of course, related to the vastly differing oxygen contents of the feed coals.

These results are similar to data reported by Campbell (1) for the slow ($3.3^\circ\text{C}/\text{min}$) pyrolysis of 50-gram samples of 6 x 12 mesh Wyodak coal, although his total yields of light hydrocarbons were greater than those reported here.

The values found by fitting the Gaussian distributed activation energy model to the data are listed on Table 2. Except for the CO data, which are clearly bimodal, the single Gaussian distribution provides a reasonable first approximation of the data. Except for the Pittsburgh Seam bituminous coal (which yielded very little CO and CO_2), the mean activation energies increase in the order CO_2 , CO (first peak), CH_4 , CO (second peak), and H_2 . The surprising result is the close correspondence of the values obtained for both E_0 and σ for each component from coals of widely differing rank. This suggests that the major mechanisms for the production of these materials are the same for all of the coals.

Table 3 lists, for comparative purposes, the parameters obtained by Campbell by fitting his data to one to three first-order reactions per compound. Since σ is zero in this model, it is necessary to allow k_i for each reaction to vary. The result is a set of extremely low values for both k_i and E_i for all of the reactions. For example, Campbell's value of E_i for hydrogen production is 19.5 kcal/g mole, compared to the E_0 's of 73 to 75 kcal/mol in Table 2, and a typical value (1) of 88 kcal/mol for C-H bond breakage. The small absolute values of k_i and E_i in Campbell's model result from fitting a yield distribution which is spread broadly over temperature with a small number of reactions.

The effect of temperature on flash pyrolysis yields has been studied by Suuberg et al. (2) for a Montana lignite. Suuberg's results (Figures 6 and 7), which are total yield data for heating small (15 mg) samples at 1000°C/sec to the indicated peak temperature, and then cooling immediately at a rate of 200°C/sec, show the same trends in the order of the appearance of the various species as do the slow pyrolysis data; in addition, Suuberg's ultimate yields of each of the light gases are similar to those observed upon slow pyrolysis of lignite and subbituminous coal in our experiments.

Suuberg also fit his results using a small number of first-order reactions to describe the yields of each species; his parameters are shown in Table 4. Reasonable values of E_0 were obtained, but the predicted yield curves, as shown on Figures 6 and 7, are notably stepwise in appearance. Also plotted on Figures 6 and 7 are the curves obtained by using the lignite pyrolysis parameters of Table 2, and the distributed activation energy model, to predict the flash pyrolysis yields. The predictions fit the data almost as well as Suuberg's own model, provided only that V_i^* for each species is allowed to vary. This illustrates the ability of the distributed activation energy model to fit both slow and fast pyrolysis data with the same values for the activation energy parameters. In contrast, the slow pyrolysis parameters reported by Campbell would predict almost no reaction under Suuberg's conditions, since his values of k_i are too small to permit any significant reaction in a time of the order of one second.

Finally, the problem inherent in applying Suuberg's model and parameters to slow pyrolysis rate data is illustrated - for the case of CO₂ formation from lignite - by Figure 8. The use of a small number of individual equations requires that the products appear in a few sharply defined peaks (corresponding to the steep steps in the yield curves) in contrast to the broadly distributed slow pyrolysis data.

CONCLUSIONS

A first-order model with distributed activation energies has the potential for explaining the effect of heating rate on the primary production of light gases (H₂, CO, CO₂, CH₄) during the devolatilization of coal; models based on small sets of first-order reactions with nondistributed activation energies do not have this potential. The activation energy distributions for the production of these species obtained from atmospheric-pressure pyrolysis, under inert atmosphere, are remarkably insensitive to coal rank. Data on identical samples of coal, over a wide range of heating rates, would be needed to confirm the validity of this approach to understanding pyrolysis kinetics.

ACKNOWLEDGEMENTS

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APPENDIX

Extension of Model Beyond Heating Period

The time-temperature history of much of the published data on coal pyrolysis may be divided into three regions:

1. Heat-up at a constant rate, m_1 , to a peak temperature, T_1 .
2. Holding at temperature, T_1 , for a time, t_H .
3. Cooling at a constant rate, m_3 (often slower than the heating rate), until the reactions are quenched.

Under these conditions, the basic first-order rate equation for a single reaction,

$$\frac{dV_i}{dt} = k (V_i^* - V_i) e^{-\frac{E}{RT}},$$

may be integrated, subject to the approximation $E/RT \approx 1$, to yield

$$\frac{V_i^* - V_i}{V_i^*} = \exp \left\{ -k \left[\frac{RT_1^2}{E} \left(\frac{1}{m_1} + \frac{1}{m_3} \right) + t_H \right] e^{-\frac{E}{RT}} \right\}$$

where V_i is now the total yield from the reaction.

For the distributed activation energy model, the corresponding equation is

$$\frac{V_i^* - V_i}{V_i^*} = \frac{1}{\sigma \sqrt{2\pi}} \int_0^{\infty} \exp \left\{ -k_0 \left[\frac{RT_1^2}{E} \left(\frac{1}{m_1} + \frac{1}{m_3} \right) + t_H \right] e^{-\frac{E}{RT}} \right\} \cdot \exp \left\{ -\frac{(E-E_0)^2}{2\sigma^2} \right\} dE$$

This latter equation may be applied to the yield of any individual component, provided that the yield can be approximated by the assumed Gaussian distributions.

In the event that a more complex time-temperature history is followed (e.g., if m_1 and m_3 are not constants), then recourse may always be had to numerical methods for calculating the final integrated yield from the model.

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TABLE 1

ANALYSIS OF COALS

ASTM Rank	State	Ultimate Analysis (% Dry)					
		C	H	N	S	Ash	O (By Difference)
Lignite	ND	61.6	4.1	1.1	0.6	10.0	22.6
Lignite	TX	64.5	4.2	1.4	0.9	10.0	19.0
Subbituminous	WY	66.4	4.6	1.0	0.8	6.0	21.2
HVC Bituminous	IL	66.4	4.6	1.1	4.5	10.6	12.8
HVA Bituminous	PA	80.5	5.0	1.2	1.1	5.0	7.2

TABLE 2
KINETIC PARAMETERS

Component	Parameter ⁺	Coals				
		North Dakota Lignite	Texas Lignite	Wyodak	Illinois No. 6	Pittsburgh
H ₂	E ₀ , kcal/mol	72.8	76.9	73.1	73.7	74.6
	σ ₀ , kcal/mol	8.8	9.8	8.0	8.6	8.2
	ν [*]	0.010	0.009	0.009	0.010	0.011
CO (1st Peak)	E ₀ , kcal/mol	51.9	52.2	50.8	--	--
	σ ₀ , kcal/mol	7.8	6.8	6.0	--	--
	ν [*]	0.025	0.018	0.022	--	--
CO (2nd Peak)	E ₀ , kcal/mol	70.3	72.7	71.2	66.7	71.1
	σ ₀ , kcal/mol	6.5	5.1	7.5	13.4	11.6
	ν [*]	0.043	0.036	0.053	0.038	0.021
CO ₂	E ₀ , kcal/mol	48.9	53.0	50.3	55.6	61.8
	σ ₀ , kcal/mol	9.5	11.4	9.6	14.2	18.1
	ν [*]	0.134	0.123	0.100	0.040	0.015
CH ₄	E ₀ , kcal/mol	57.7	60.1	58.2	58.8	58.7
	σ ₀ , kcal/mol	6.0	7.0	5.9	5.8	4.8
	ν [*]	0.016	0.021	0.021	0.022	0.030
Total Weight Loss	E ₀ , kcal/mol	52.7	52.5	53.2	53.0	51.8
	σ ₀ , kcal/mol	11.3	10.0	9.7	9.3	5.7
	ν [*]	0.40	0.40	0.41	0.34	0.30

⁺k₀ is fixed at 10¹⁵ min⁻¹ in all cases.

TABLE 3
CAMPBELL'S PARAMETERS FOR WYODAK COAL

<u>Component</u>	<u>E₀, kcal/mol</u>	<u>k₀, min⁻¹</u>	<u>V*, g/g coal</u>
H ₂	22.3	1200	0.0102
CO, Reaction 1	18.0	3300	0.016
Reaction 2	30.1	1.5 x 10 ⁵	0.037
CO ₂ , Reaction 1	19.5	3.3 x 10 ⁴	0.055
Reaction 2	23.0	1.4 x 10 ⁴	0.047
CH ₄ , Reaction 1	31.1	1.0 x 10 ⁷	0.014
Reaction 2	31.1	1.7 x 10 ⁶	0.016
Reaction 3	35.4	1.8 x 10 ⁶	0.014

TABLE 4
SUUBERG'S PARAMETERS FOR NORTH DAKOTA LIGNITE

<u>Component</u>	<u>E₀, kcal/mol</u>	<u>k₀, min⁻¹</u>	<u>V*, g/g coal</u>
H ₂	88.8	9.5 x 10 ¹⁹	0.0050
CO, Reaction 1	44.4	1.1 x 10 ¹⁴	0.0177
Reaction 2	59.5	1.6 x 10 ¹⁴	0.0535
Reaction 3	58.4	3.5 x 10 ¹¹	0.0226
CO ₂ , Reaction 1	36.2	1.3 x 10 ¹³	0.0570
Reaction 2	64.3	3.5 x 10 ¹⁵	0.0270
Reaction 3	42.0	3.3 x 10 ⁸	0.0109
CH ₄ , Reaction 1	51.6	9.7 x 10 ¹⁵	0.0034
Reaction 2	69.4	2.8 x 10 ¹⁶	0.0092

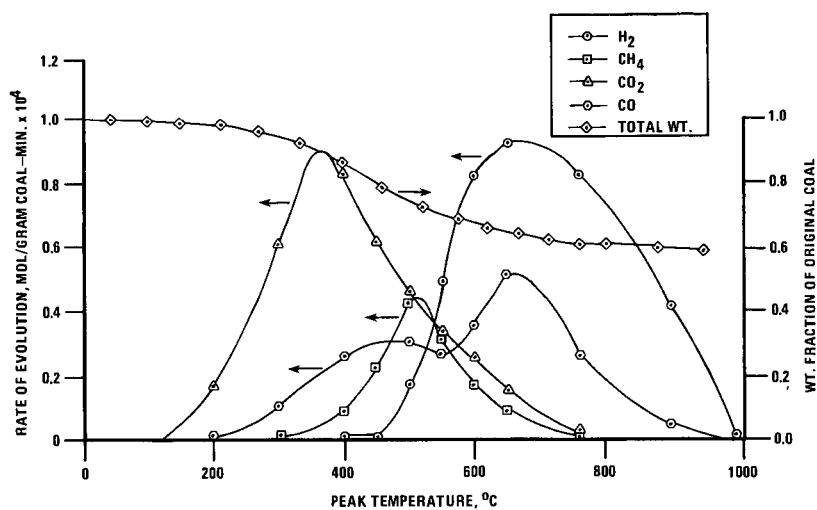


FIGURE 1.
PYROLYSIS YIELDS FROM A NORTH DAKOTA LIGNITE

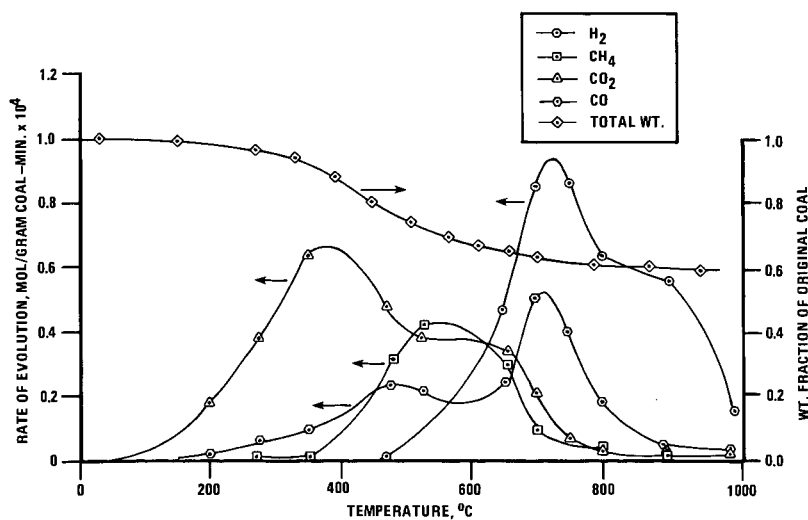


FIGURE 2.
PYROLYSIS YIELDS FROM A TEXAS LIGNITE

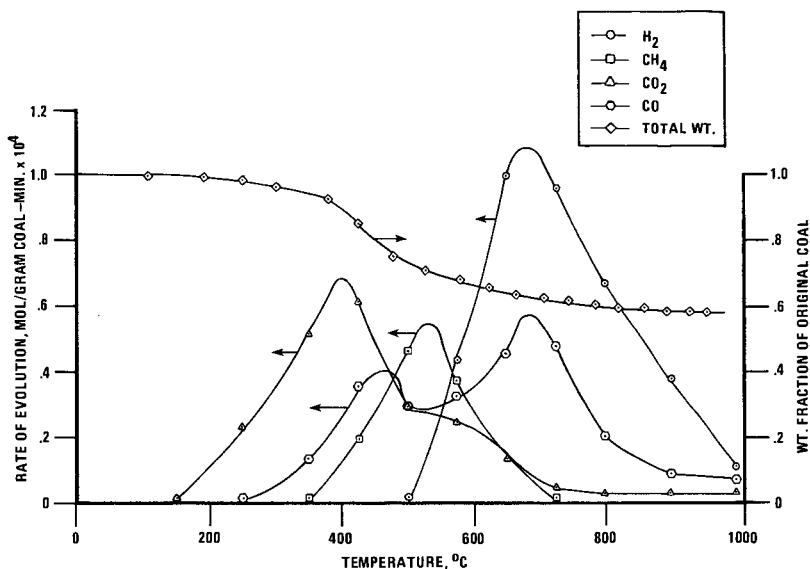


FIGURE 3.
PYROLYSIS YIELDS FROM A WYODAK COAL

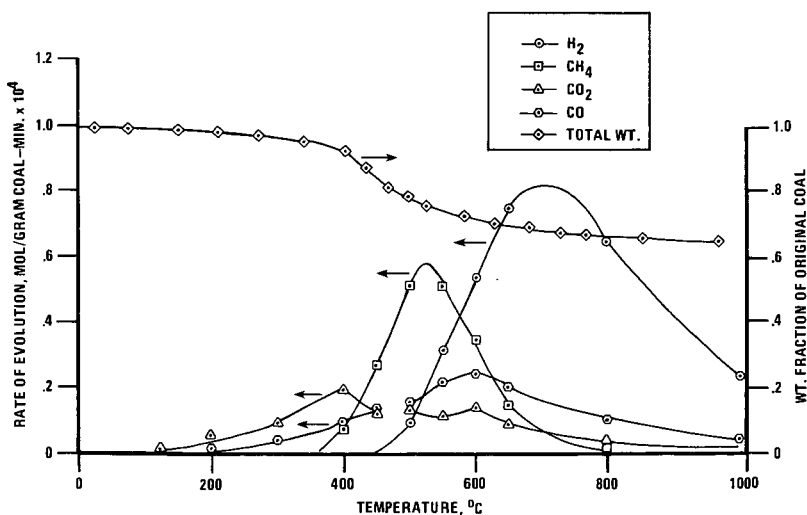


FIGURE 4.
PYROLYSIS YIELDS FROM AN ILLINOIS NO. 6 COAL

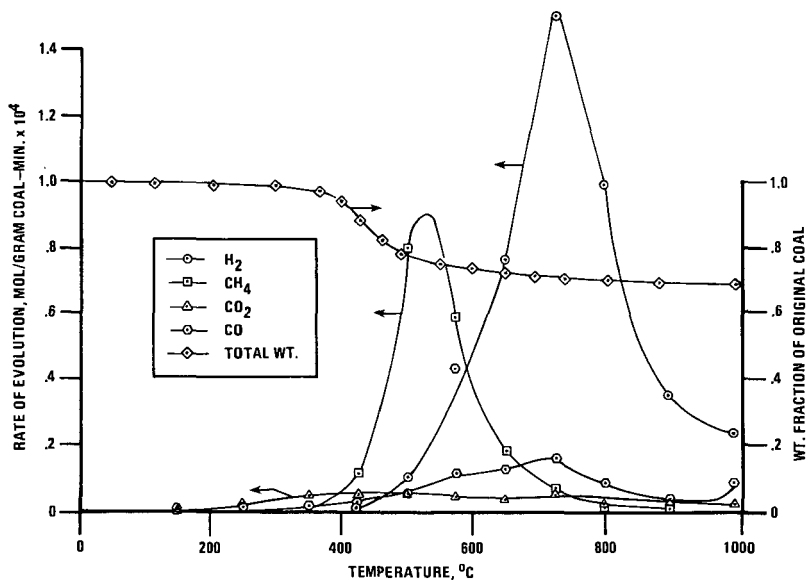


FIGURE 5.
PYROLYSIS YIELDS FROM A PITTSBURGH SEAM COAL

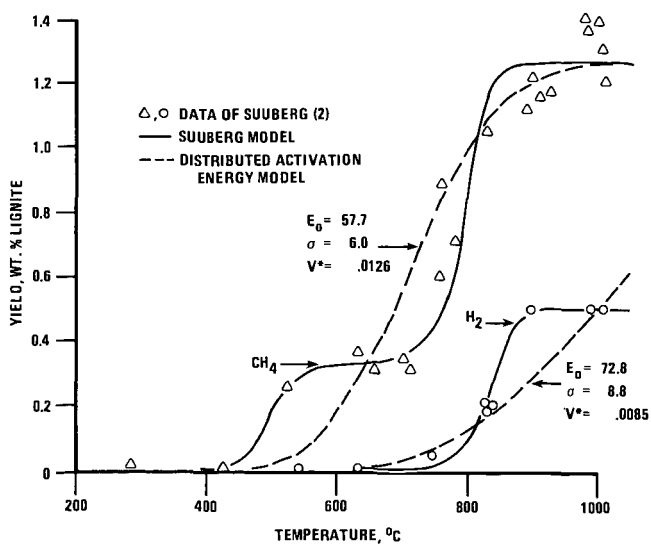


FIGURE 6.
YIELDS OF METHANE AND HYDROGEN VIA FLASH
PYROLYSIS OF MONTANA LIGNITE

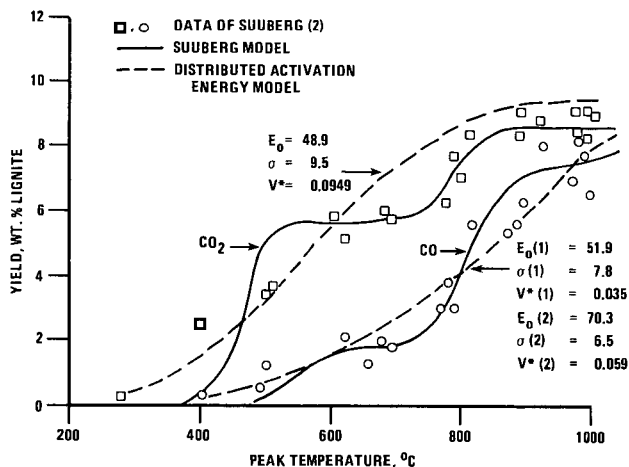


FIGURE 7.
 YIELDS OF CO AND CO₂
 VIA FLASH PYROLYSIS OF MONTANA LIGNITE

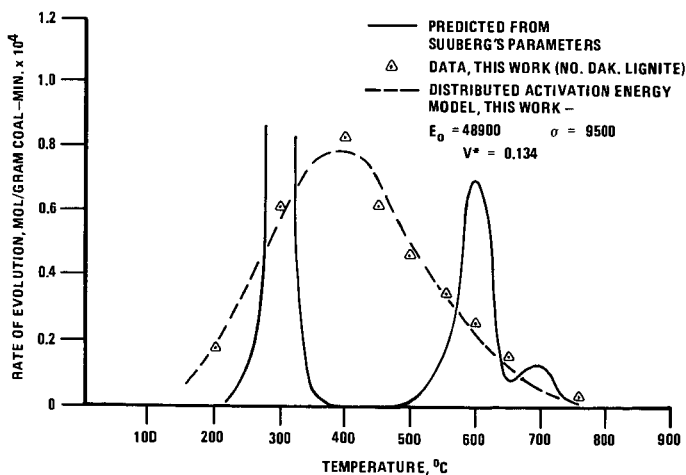


FIGURE 8.
 CO₂ PRODUCTION RATE
 VIA SLOW PYROLYSIS OF LIGNITES

A MODEL FOR COAL PYROLYSIS

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INTRODUCTION

Pyrolysis of coal occurs in all coal conversion processes and is perhaps the most difficult to model mathematically. A number of models on coal pyrolysis have been proposed during the past several decades. However, very few of these models address the simultaneous changes in product distribution and particle weight loss (or conversion) over a wide range of operating conditions. Such a mathematical model which could take into consideration the effects of residence time, final temperature, heating rate and pressure is needed for design and scale-up of coal pyrolysis and gasification reactors. The purpose of this study is to develop such a mathematical model for simulation of the pyrolysis phenomena of a coal particle. The model to be developed should be general enough to be applicable to other pyrolysis system such as the pyrolysis of wood.

MODEL DEVELOPMENT

The assumptions used to formulate the single particle model are as follows:

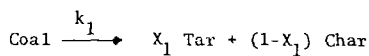
- (a) pseudo-steady state concentration profiles
- (b) negligible increase in internal pressure
- (c) equal binary diffusivities

This model combines the chemical reactions and the transport processes occurring during pyrolysis.

1. Chemical Reactions:

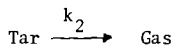
Three chemical reactions are assumed to simultaneously occur within a coal particle which is undergoing pyrolysis in an inert atmosphere. These are devolatilization, cracking and deposition. For convenience, the products of pyrolysis are categorized as char, tar and gas. Char is defined as the undistillable material which remains in the form of a solid. Tar is defined as the distillable liquid which has a molecular weight larger than C_6 . Gas is defined as those components lighter than C_6 , i.e., CO , CH_4 , CO_2 , C_2H_6 , H_2O , etc. Both tar and gas occur in the form of vapor when coal is pyrolyzed. A similar treatment was applied to the catalytic cracking of petroleum⁽¹¹⁾. During pyrolysis all of the chemical reactions are assumed to be first order with respect to the concentration of reactants and rate constants are expressed in Arrhenius form. The chemical reactions and the rate expressions for the pyrolysis of a coal particle are formulated as follows:

A. Devolatilization



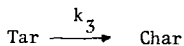
$$\text{Rate} = k_{10} \cdot \exp(-E_1/\overline{RT}) C_{\text{coal}}$$

B. Cracking



$$\text{Rate} = k_{20} \cdot \exp(-E_2/\overline{RT}) C_{\text{tar}}$$

C. Deposition



$$\text{Rate} = k_{30} \cdot \exp(-E_3/\overline{RT}) C_{\text{tar}}$$

The net production rates of tar, gas and inert gas can be obtained as:

$$R_{\text{tar}} = X_1 k_1 C_{\text{coal}} - (k_2 + k_3) C_{\text{tar}} \quad (1)$$

$$R_{\text{gas}} = k_2 C_{\text{tar}}$$

and $R_{\text{inert gas}} = 0$

While the solid concentrations, C_i , and the net production rates of coal and char can be obtained as:

$$\frac{dC_i}{dt} = R_i \quad (2)$$

where

i is the coal or char

and

$$R_{\text{coal}} = -k_1 C_{\text{coal}}$$

$$R_{\text{char}} = (1-X_1)k_1 C_{\text{coal}} + \frac{1}{(\frac{4}{3} \pi R^3)} \int_0^R k_3 C_{\text{tar}} 4\pi r^2 dr$$

2. Transport Processes:

Both mass and heat transfer affect the pyrolysis of a single coal particle. This is particularly significant for large particles.

2-1. Mass transfer

A. Gas phase

The coal particle can be considered as a porous sphere which retains its integrity as the pyrolysis reaction proceeds. The conservation equation for the gaseous species, i , tar, gas or inert gas, inside the particle having a mass concentration, C_i , can be formulated as⁽⁸⁾:

$$\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 N_i) = R_i \quad (3)$$

where R_i is the rate of generation of the species i due to the chemical reactions.

N_i is the mass flux of the species i and can be expressed as the sum of the diffusion flux in the radial direction and the bulk flow through the pores. Thus

$$N_i = -D_{\text{eff},i} \frac{\partial C_i}{\partial r} + \bar{W}_i \sum_j N_j \quad (4)$$

\bar{W}_i , the weight fraction of the species i in the gas phase, can be expressed as:

$$\bar{W}_i = C_i / \sum_j C_j \quad (5)$$

B. Gas film

The conservation equation for the gaseous species, i (tar, gas or inert gas) across the gas film can be written as:

$$N_i \big|_R = k_{gi} [C_{i,s} - C_{i,b}] \quad (6)$$

where,

$C_{i,s}$ and $C_{i,b}$ are the concentrations of species i at the particle surface and at the bulk gas stream outside, respectively.

k_{gi} is the mass transfer coefficient across the gas film and can be estimated from an appropriate mass transfer correlation.

2-2. Heat transfer

The energy balance equation for the particle is derived by taking into account convective, radiative and conductive heat transfer with the heating devices and the heat of reaction of the pyrolysis process. The temperature gradient which occurs inside of the particle due to the conduction is negligible for small particles and is neglected. (For a 1000 μm particle, the maximum temperature gradient is 20 °C at 0.5 sec and less than 5 °C at 1 sec. This is the case, if the particle at room temperature is dropped into a pyrolyzer maintained at 1000 °C. The heating rate of the particle is 1000 °C/sec which is in the range usually encountered in pyrolyzers or gasifiers). Accordingly,

$$C_{ps} \cdot \rho_s \cdot \frac{dT}{dt} = \frac{3}{R} h_c (T_w - T) + \frac{3\sigma Fe}{R} (T_w^4 - T^4) + \frac{3 k a}{R^2} (T_w - T) + \sum_i (-\Delta H_i) R_i \quad (7)$$

where, a represents the fraction of the surface area of the particle that comes in contact with the heating elements. T_w is the temperature of the heating elements and can be characterized by the following equation:

$$C_{pw} \cdot \rho_w \cdot \frac{dT_w}{dt} = h'_{ov} (T_f - T_w) \quad (8)$$

Since the heating rate of a heating device is specified in the experimental work the wire temperature, T_w , can be obtained by substituting a relative overall heat transfer coefficient, h'_{ov} , into Equation 8.

DETERMINATION OF PARAMETERS

Sensitivity analysis of each parameter of the model on the weight loss of the particle under different operating conditions shows that the value of k_1 for different types of coal can be estimated by comparing the weight loss history, the value of k_2 can be estimated based on product distribution of tar and gas under different temperatures and the value of k_3 can be estimated based on the pressure effect on the weight loss.

The pyrolysis data of Anthony and Howard^(1,2,3) for bituminous coal and those of Suuberg et al.⁽¹⁰⁾ for lignite coal were used to determine the reaction rate constants for the devolatilization step and the deposition step. For sub-bituminous coal, due to the lack of data on weight loss history and pressure effects, an average value between the rate constant of bituminous coal and that of lignite is used. The cracking reaction rate constants for each type of coal were chosen based on the product distribution data of Solomon et al.⁽⁹⁾. The reaction rate constants obtained for different ranks of coals are tabulated in Table 1.

A comparison between the calculated results and the experimental data for the weight loss history and the effect of pressure on bituminous coal is shown in Figure 1 and 2. The effect of pressure on weight loss for lignite has been reported to be negligible for pressures ranging from 0.01 to 100 atmospheres⁽³⁾. Figure 2 also demonstrates this trend. Figure 3 shows the effect of the heating rate on the weight loss history for lignite. Good agreement between the calculated lines and the experimental data indicates that the proposed model can represent the pyrolysis process successfully. The comparisons of the product distribution of tar and gas are shown in Figures 4, 5, and 6 for bituminous, sub-bituminous and lignite coal, respectively. The calculated tar yield is slightly higher than the observed yield especially in the low temperature range. Figures 7 to 9 show the application of the model with the predetermined reaction rate constants for bituminous, sub-bituminous and lignite coal. X_1 , the amount of tar formed in the devolatilization step, is correlated with the volatile matter content for each type of coal and is shown in Figure 10. The correlation equations for X_1 with different types of coals can be seen to represent this value closely for bituminous coal. This results from the aforementioned lack of data necessary for accurately determining the chemical reaction rate constants. The relation of X_1 with volatile matter content (dry ash free basis) are listed below:

$$\text{Bituminous } X_1 = 1.3 \text{ (V.M.)} + 0.025 \quad (9)$$

$$\text{Lignite } X_1 = 0.95 \text{ (V.M.)} + 0.025 \quad (10)$$

DISCUSSION AND CONCLUSIONS

Although the rate of heating affects the weight loss history of lignite coal as shown in Figure 3, it appears that the ultimate weight loss is not affected by the heating rate over the range between 650 to 10^4 °C/sec. However, Badzioch and Hawksley⁽⁴⁾ reported the ultimate weight loss of the particle at a rapid heating rate ($>2.5 \times 10^4$ °C/sec) may be 1.2 to 1.4 times higher than that at slow heating rate ($< 1/20$ °C/sec). There is a concern that their results might be attributable to the experimental conditions employed to achieve the rapid heating rate by use of small particles in an entrained reactor. For a slow heating rate, the ultimate weight loss is approximately the same as the proximate volatile matter content of the coal⁽⁵⁾. Additional studies are needed to clarify the effect of heating rate on the ultimate weight loss.

The estimation of the amount of tar formed at low temperatures based on the model is higher than those observed experimentally. This is shown in Figures 4 to 6. A minor adjustment was attempted in the cracking reaction rate constants, but this did not improve on the result. Hence, the model cannot adequately represent the pyrolysis at low temperatures ($< 600^\circ\text{C}$).

The weight loss curves at different temperatures for bituminous, sub-bituminous and lignite coals show that the calculated weight loss of the particle at temperatures higher than 800°C tends to peak rather than continuously increase as seen in some of the experimental data. The validity of the model above 1000°C is still undetermined due to the lack of experimental data above this temperature.

The phenomena of coal pyrolysis between bituminous and lignite coals are apparently quite different. Bituminous coal is more pressure dependent and has a lower proportion of gas in the pyrolysis products than lignite. The effect of pressure on the weight loss, according to the model, is primarily related to the rate of tar deposition. Since the rate of tar deposition is higher for the bituminous coal compared to that of lignite, the effect of pressure on the weight loss during pyrolysis is also more appreciable for bituminous coal than lignite. Furthermore, the ratio of the cracking rate to the deposition rate has an important effect on the amount of gas and tar formed. Since this ratio is greater for lignite than bituminous coal, lignite produces more gas than bituminous coal under similar pyrolytic conditions. This implies that the fraction of tar formed during the devolatilization step, X_1 , is smaller for lignite than that for bituminous coal as indicated by Equations 9 and 10.

The model developed is applicable within the operating range of pyrolysis process listed below:

$$400^\circ\text{C} < \text{Temperature} < 1000^\circ\text{C}$$

$$25 \mu\text{m} < \text{Particle size} < 1000 \mu\text{m}$$

$1/180 \text{ } ^\circ\text{C/sec} < \text{Heating rate} < 10^4 \text{ } ^\circ\text{C/sec}$

$0.01 \text{ atm} < \text{Pressure} < 100 \text{ atm}$

For large particles beyond 1000 μm , temperature gradient within the particle may not be neglected requiring an additional term on heat condition within the particle to be included in Equation 7.

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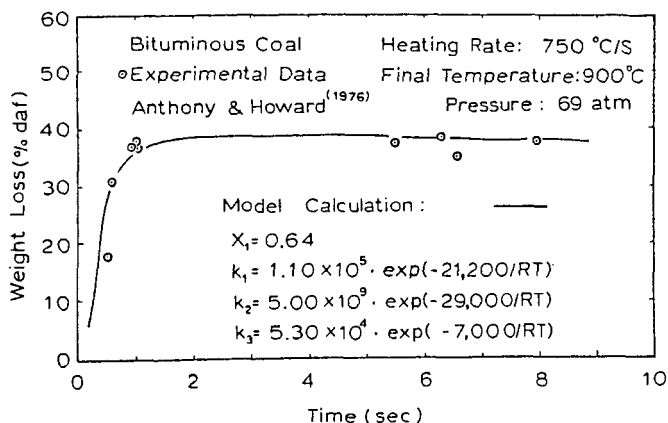


FIG. 1. PYROLYSIS WEIGHT LOSS HISTORY OF BITUMINOUS COAL

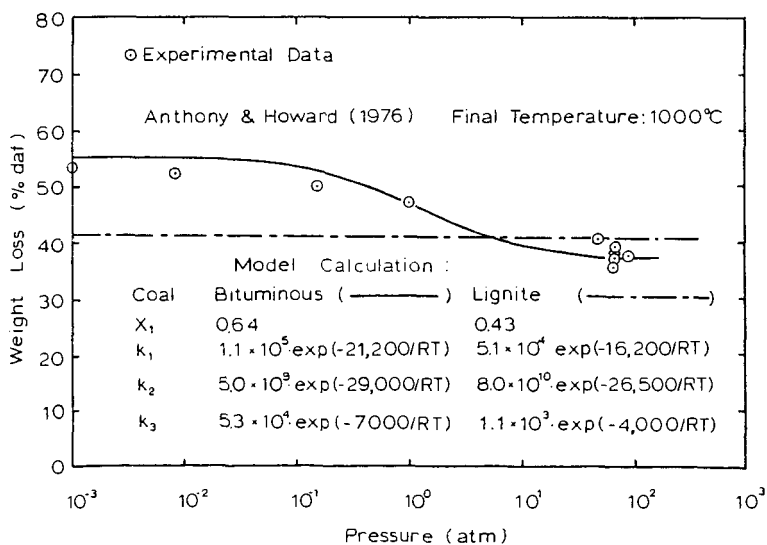


FIG. 2. EFFECT OF PRESSURE ON THE WEIGHT LOSS OF BITUMINOUS AND LIGNITE COALS

Table 1
Reaction Rate Constants for Coal Pyrolysis Model

Reaction Rate Constants	Coal	Bituminous	Sub-bituminous	Lignite
k_{10} 1/sec		1.1×10^5	7.5×10^4	5.1×10^4
E_1 J/mole cal/gmole		88,700 21,200	78,200 18,700	67,800 16,200
k_{20} 1/sec		9.7×10^9	3.5×10^{10}	8×10^{10}
E_2 J/mole cal/gmole		121,500 29,000	116,100 27,750	110,900 26,500
k_{30} 1/sec		5.3×10^4	2.5×10^4	1.1×10^3
E_3 J/mole cal/gmole		29,300 7,000	23,000 5,500	16,700 4,000

Uncertainty of E_i : ± 100 J/mole or cal/gmole

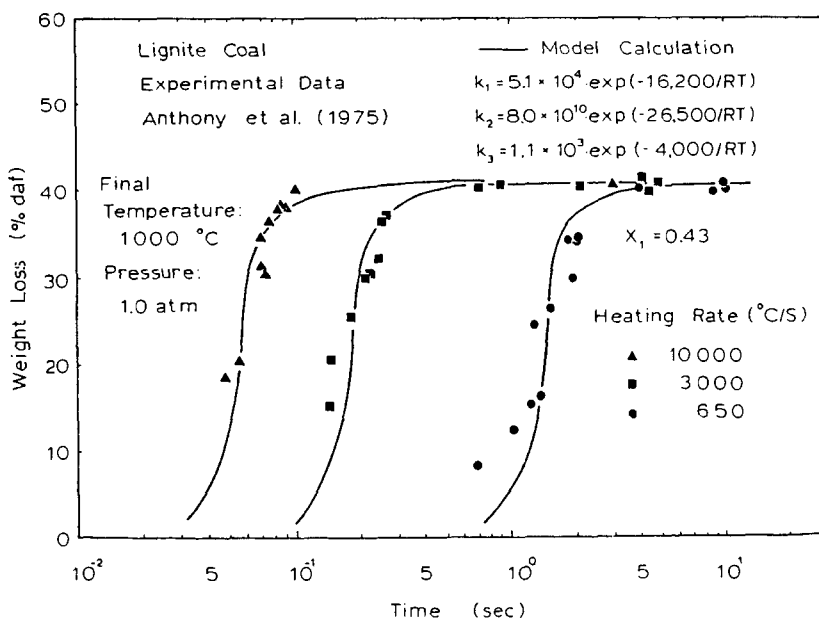


FIG. 3. EFFECT OF HEATING RATE ON THE WEIGHT LOSS HISTORY OF LIGNITE COAL

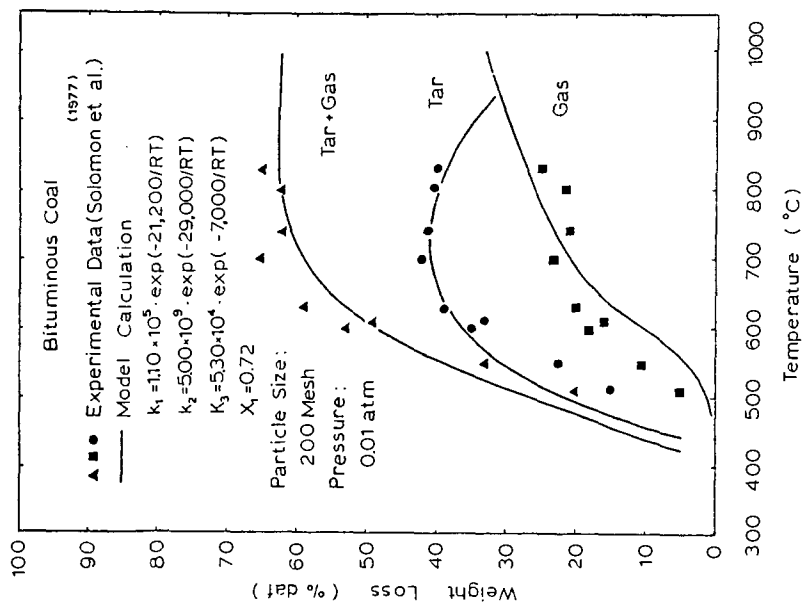


FIG. 4. PRODUCT DISTRIBUTION FROM BITUMINOUS COAL PYROLYSIS

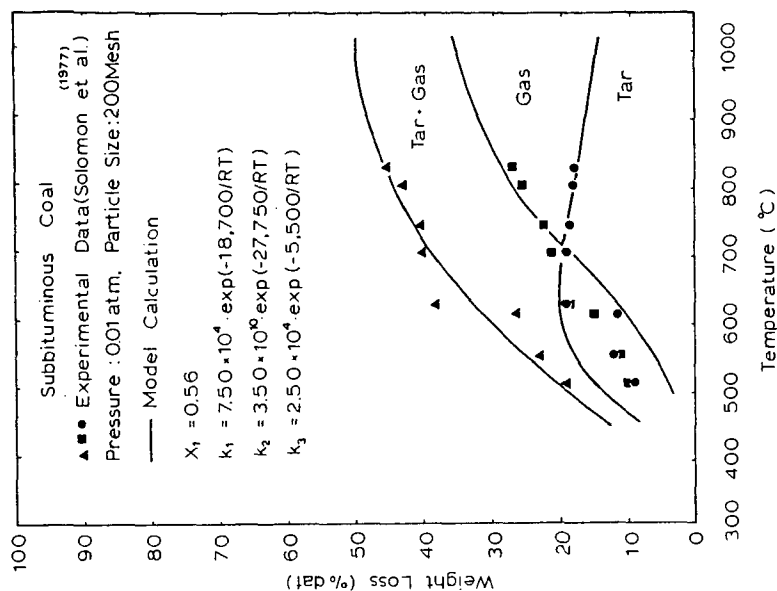


FIG. 5. PRODUCT DISTRIBUTION FROM SUB-BITUMINOUS COAL PYROLYSIS

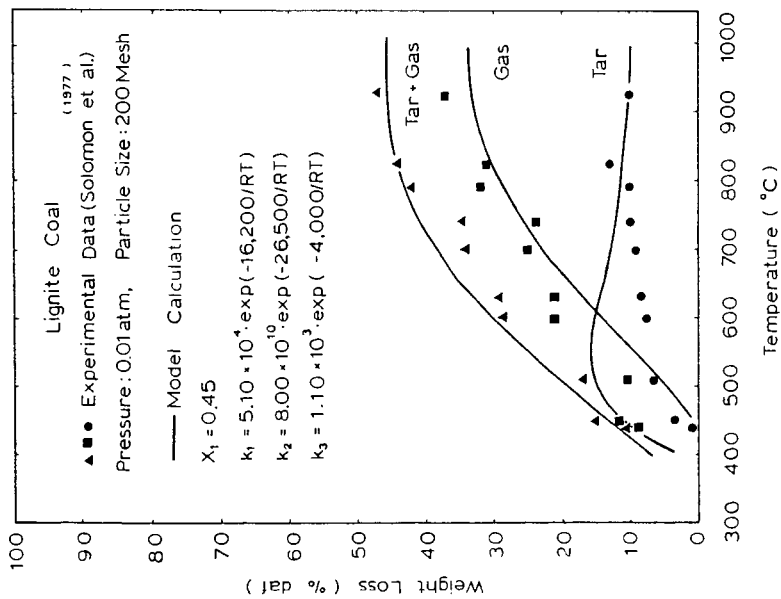


FIG. 6. PRODUCT DISTRIBUTION FROM LIGNITE COAL PYROLYSIS

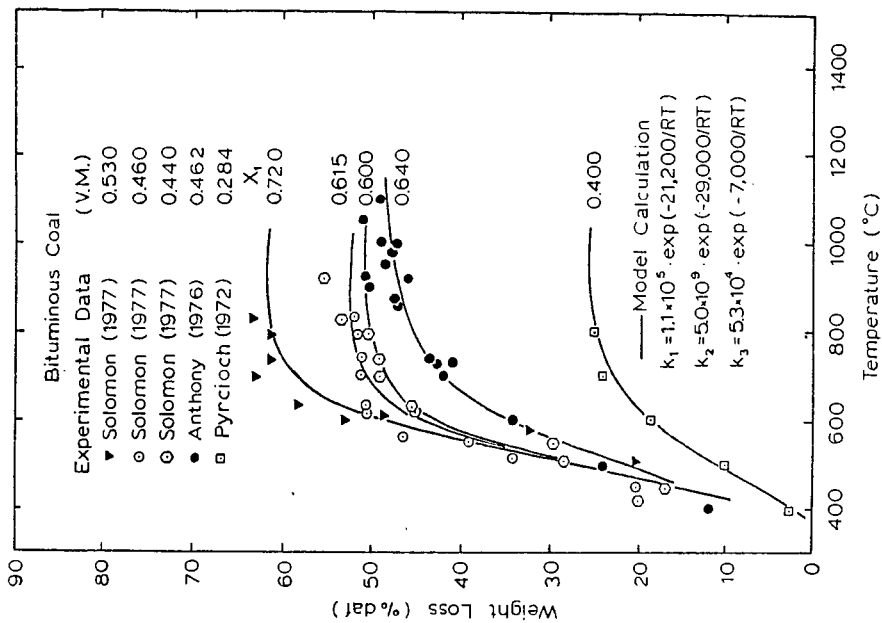


FIG. 7. EFFECT OF TEMPERATURE ON THE WEIGHT LOSS OF BITUMINOUS COAL

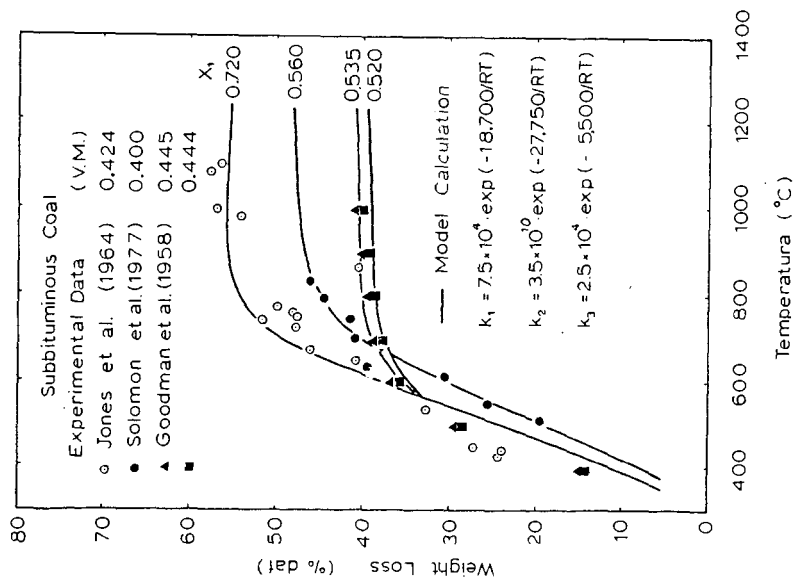


FIG. 8. EFFECT OF TEMPERATURE ON THE WEIGHT LOSS OF SUB-BITUMINOUS COAL

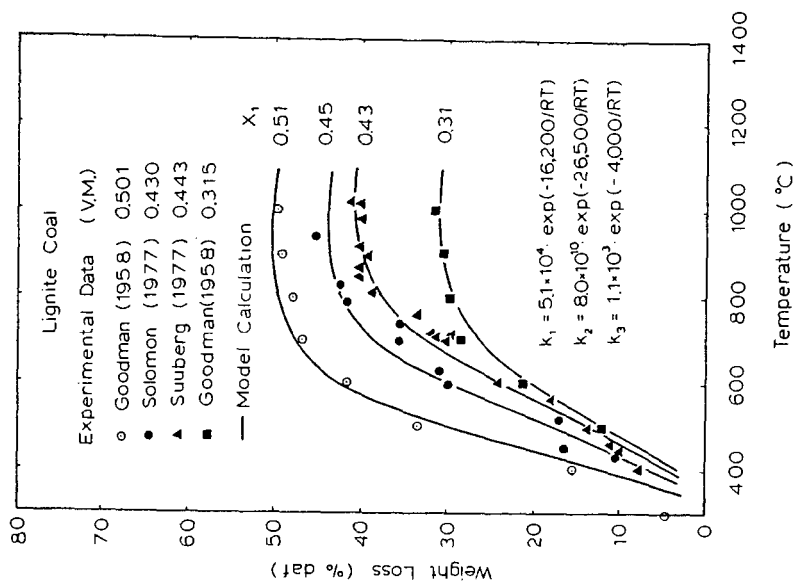


FIG. 9. EFFECT OF TEMPERATURE ON THE WEIGHT LOSS OF LIGNITE COAL

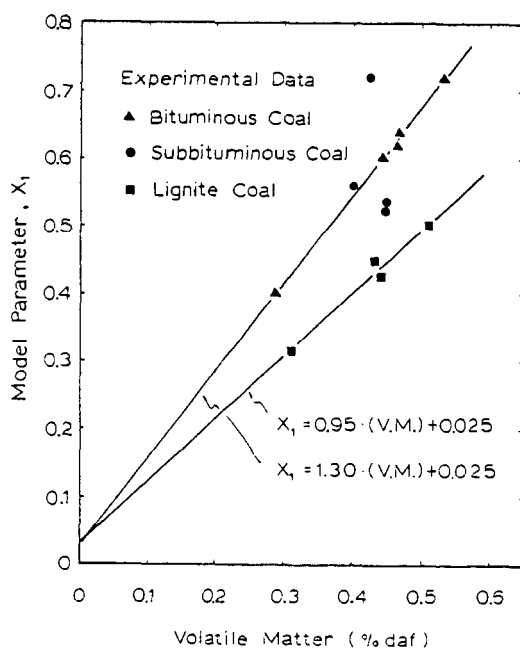


FIG. 10. THE RELATION OF THE MODEL PARAMETER, X_1 , WITH THE VOLATILE MATTER CONTENT FOR BITUMINOUS, SUB-BITUMINOUS AND LIGNITE COALS

MATHEMATICAL MODEL OF BITUMINOUS COAL PYROLYSIS--TAR FORMATION AND EVOLUTION. M.W. Zacharias and J.B. Howard. Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

A mathematical model of the rapid pyrolysis of caking coal has been fitted to extensive data on a Pittsburgh Seam coal pyrolyzed under wide ranges of conditions in a laboratory batch-sample reactor. The model includes an improved description of the role of mass transfer and secondary reactions and offers a means for the prediction of pressure effects on product yields. According to the model, a coal particle decomposes to form tar, lighter volatiles and char. The primary tar may evaporate and diffuse away from the particle or undergo secondary reactions leading to lighter volatiles and coke. The model is quite successful in predicting tar yields at pressures ranging from vacuum to 69 atm, although the predictions at the highest pressure are lower than the experimental yields, particularly at low temperatures. Possible explanations for this discrepancy will be presented. Results from application of the model indicate that mass transfer limitations are negligible under vacuum conditions. As the pressure is increased, tar evolution becomes limited by diffusion into the bulk reactor gas.

EXPERIMENTAL STUDY AND MODELING OF COAL PYROLYSIS AT HIGH TEMPERATURES*

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INTRODUCTION

In a recent study, the vacuum pyrolysis behavior of a lignite and twelve bituminous coals was measured over the range 300 to 1000°C (1,2,3). The results were successfully simulated using a model which predicts the time and temperature dependent product evolution from a knowledge of the function group composition of the coal and a general set of kinetic rates which vary with evolved product but not with coal type.

This paper reports the extension of this investigation to temperatures up to 1450°C and to a wider number of measured and modeled pyrolysis products. Experiments have been performed in an apparatus which employs a Fourier Transform Infrared Spectrometer (FTIR) for on-line analysis of gas species. The FTIR allows the direct accumulation of release rate data for major species by monitoring the gas concentration during a pyrolysis run. Results have been obtained with a Pittsburgh seam bituminous and a Montana lignite. The temperature dependent evolution of corresponding products are similar for the two coals indicating that the use of coal independent kinetic rates is applicable for the additional products and higher temperatures. The dominant effect observed at higher temperatures is the trend toward increased yields of hydrogen gas and unsaturated compounds (olefins, acetylene and probably soot) at the expense of paraffins. These effects are being modeled by including additional parallel reaction paths for the decomposition of the aliphatic content of the coal.

EXPERIMENTAL

The apparatus is illustrated in Fig. 1. It consists of a small chamber in which the coal is pyrolyzed connected through a glass wool filter to a large gas cell for infrared analysis. The coal is evenly distributed between the folds of a stainless steel, molybdenum or tungsten screen and a current is passed through the screen to heat the coal. Coal temperatures of 1450°C and heating rates of 2000°C/sec were achieved using the tungsten screen. Gas analysis is performed with a Nicolet (FTIR) which permits low resolution analysis at 0.5 second intervals. The low resolution analysis can determine CO, CO₂, H₂O, CH₄, COS, SO₂, CS₂, HCN, C₂H₂, C₂H₄, C₃H₆, benzene and heavy paraffins and olefins. A high resolution analysis made at the completion of a run can determine all of the above plus C₂H₆, C₃H₈, C₄H₈, NH₃ and potentially many other species which have not yet been observed. H₂ is determined by difference. Other features of the apparatus are similar to those described previously (1,2,3).

Calibration of the FTIR has been made using pure gases or prepared gas mixtures. Unfortunately, most of the gases of interest show a marked increase in absorbance with dilution. The explanation for this effect is that the absorption lines for these gases are extremely sharp and for moderate concentrations all the infrared energy is

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absorbed at the line center in a path shorter than the absorption cell. The instrument resolution is substantially broader than the line width so the lines do not appear to be truncated. Dilution of the gas broadens the line, reducing the absorbance at line center so that a longer path contributes to the absorptivity, thus increasing the average absorbance. This effect makes calibration of these gases in the pyrolysis gas mixture difficult. The solution has been to dilute the mixture with nitrogen to a fixed pressure at which calibrations have been made.

Figure 2 shows the spectra obtained at several time intervals during an 80 second devolatilization run at about 500°C. Kinetic rate data for major species can be determined from such scans as indicated in Fig. 3 which shows the methane yield and the pressure rise in the system as a function of time.

Pyrolysis data were obtained up to temperatures of 1450°C for a Pittsburgh seam coal (PSOC 170) and a Montana lignite. For the Pittsburgh seam coal 80 second pyrolysis runs were made with 200 mg samples at temperatures from 400 to 1000°C. For these conditions, the temperature rise takes on the order of two seconds. More rapid heating (less than one second) was achieved using smaller (50 mg) samples. Ten second pyrolysis runs were made with 50 mg samples for both coals.

RESULTS

Using the procedure shown in Fig. 3 the methane kinetic constants were determined for the 10 and 80 runs. These data are plotted in Fig. 4 along with a line for the temperature dependent kinetic rate for methane previously determined (2). As can be seen the lignite and bituminous data are quite close and all data are in reasonable agreement with the previously determined line. The high temperature points for the 80 second runs are low because of the slow heating described above and presumably the same sort of limitations are affecting the 10 second runs at the very high temperatures.

Pyrolysis data for the 10 second runs are plotted in Fig. 5. Figs 5a and b show the product distribution. Included in the light gases are all the species listed except for those heavier than C_3 , which are included with the heavier hydrocarbons (HC). An interesting feature of these data are the high volatile yields obtained at high temperatures. Volatile yields of up to 70% were observed as compared with ASTM volatile yields of 46% and 59% for the bituminous coal and lignite respectively.

Several of the gaseous species are shown in Figs. 5c-h. The similarity between lignite and bituminous coal is apparent in the temperature dependence of the evolution of each species. Figs. c to f show results for H_2 , CH_4 and C_2H_2 and heavy olefins and paraffins. These figures illustrate the tendency for high temperature pyrolysis to favor molecular hydrogen and unsaturated compounds. Figures g and h show the distribution of oxygen containing species.

PYROLYSIS MODEL

A successful model was developed to simulate the pyrolysis behavior of the thirteen coals previously studied at low temperature (1,2,3). The model assumes that large molecular fragments ("monomers") are released from the coal "polymer" with only minor alteration to form tar while simultaneous cracking of the chemical structure forms the light molecules of the gas. Any chemical component of the coal can, therefore, evolve as part of the tar or as a species in the gas. The mathematical

description presented in detail in Refs. 2 and 3 represents the coal as a rectangular area with X and Y dimensions. The Y dimension is divided into fractions according to the chemical composition of the coal. Y_i^0 represents the initial fraction of a particular component (carboxyl, aromatic hydrogen, etc) and $\sum Y_i^0 = 1$. The evolution of each component into the gas (carboxyl into CO_2 , aromatic hydrogen into H_2 , etc) is represented by the first order diminishing of the Y_i dimension, $Y_i = Y_i^0 \exp(-k_{i1}t)$. The X dimension is divided into a potential tar forming fraction X^0 and a non-tar forming fraction $1-X^0$ with the evolution of the tar being represented by the first order diminishing of the X dimension $X = X^0 \exp(-k_{\text{tar}}t)$. The amount of a particular component in the char is $(1-X^0+X)Y_i$ and the amounts in the gas and tar may be obtained by integration. It was found that a general set of kinetic constants (k_{i1} 's and k_{tar}) could be used for all the coals. The differences among coal results solely from the different mix of chemical groups (the Y_i^0 's). As described in Ref. 3 many of the Y_i^0 's may be determined from ultimate and infrared analysis.

Modifications of the model were made to include the high temperature production of unsaturated compounds. An example, the production of acetylene and H_2 is assumed to be a third independent path for the evolution of an aliphatic component. The component is represented as a volume and the evolution of acetylene and H_2 is represented by the diminishing of the X dimension, $Z = Z^0 \exp(-k_{\text{ac}}t)$ where $Z^0 = 1$. The amount of the component in the char is then $(1-X^0+X)Y_iZ$. The evolved amounts may be obtained by integration. Further competitive processes such as the production of olefins plus H_2 from paraffins and the production of soot and H_2 from aliphatics were incorporated in a like manner.

The results are the lines shown in Fig. 5. The kinetic constants are the same as those used in Ref. 2 with the exception of: $k_{\text{H}_2\text{O}} = 45 \exp(-4950/T)$, $k_{\text{al}} = 750 \exp(-8000/T)$ and the addition of: $k_{\text{ac}} = 2.19 \times 10^{10} \exp(-35000/T)$, $k_{\text{ol}} = 2.0 \times 10^7 \exp(-20000/T)$, $k_{\text{soot}} = 9.5 \times 10^{10} \exp(-35000/T)$. The model is in reasonable agreement with experiment for most species. Exceptions are H_2O and H_2 . The decrease in H_2O at high temperatures has not been modeled. The effect could be a steam char reaction to form CO and H_2 . Inclusion of this reaction would improve the agreement for CO and H_2 as well.

CONCLUSIONS

1. Using a heated grid apparatus with on-line gas analysis by FTIR, data has been obtained for a large number of pyrolysis products from a lignite and a bituminous coal at temperatures up to 1450°C .
2. The temperature dependent evolution of corresponding products from the lignite and bituminous coal vary in magnitude but are otherwise quite similar.
3. The pyrolysis behavior has been simulated by modifying a previously developed model which uses the same kinetic rates for all coals. Modifications of the model were made to include the high temperature evolution of H_2 and unsaturated compounds (olefins, acetylene, and soot) from the aliphatic material in the coal.
4. The coal parameters of the model are related to the functional group composition of the coal.

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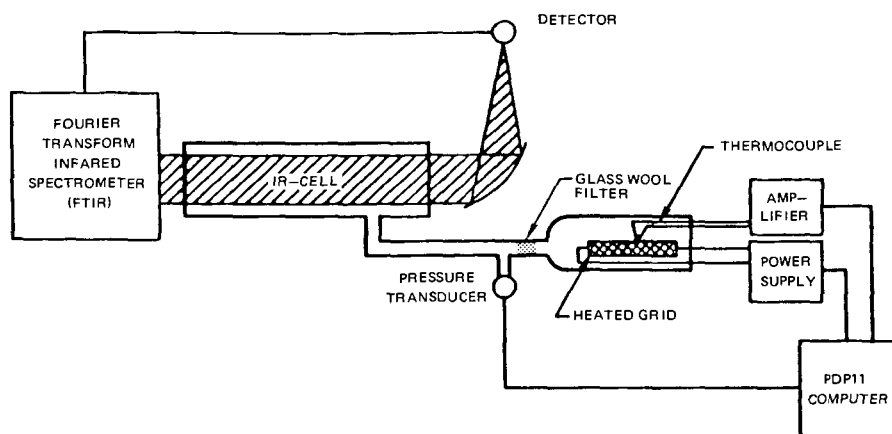


FIG. 1 PYROLYSIS APPARATUS

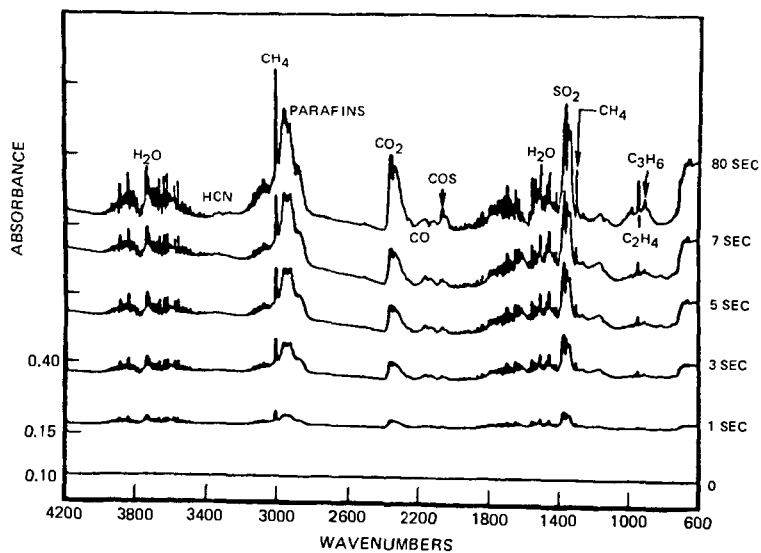


FIG. 2 INFRARED SPECTRA OF EVOLVING PYROLYSIS GAS

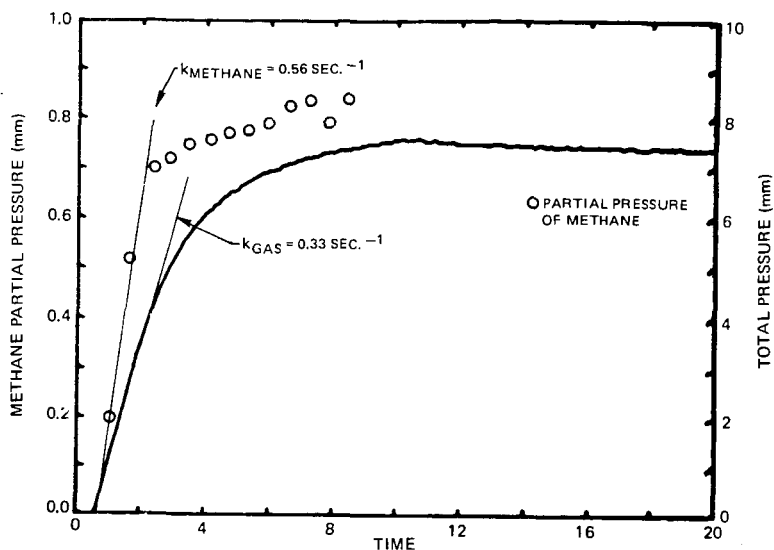


FIG. 3 TIME DEPENDENCE OF METHANE PARTIAL PRESSURE AND TOTAL PRESSURE DURING PYROLYSIS

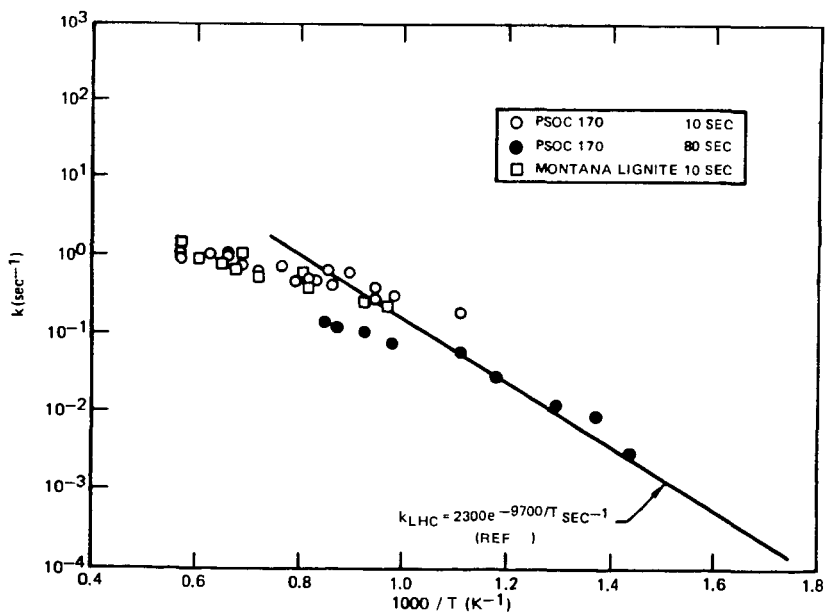


FIG. 4 RATE CONSTANT FOR METHANE EVOLUTION

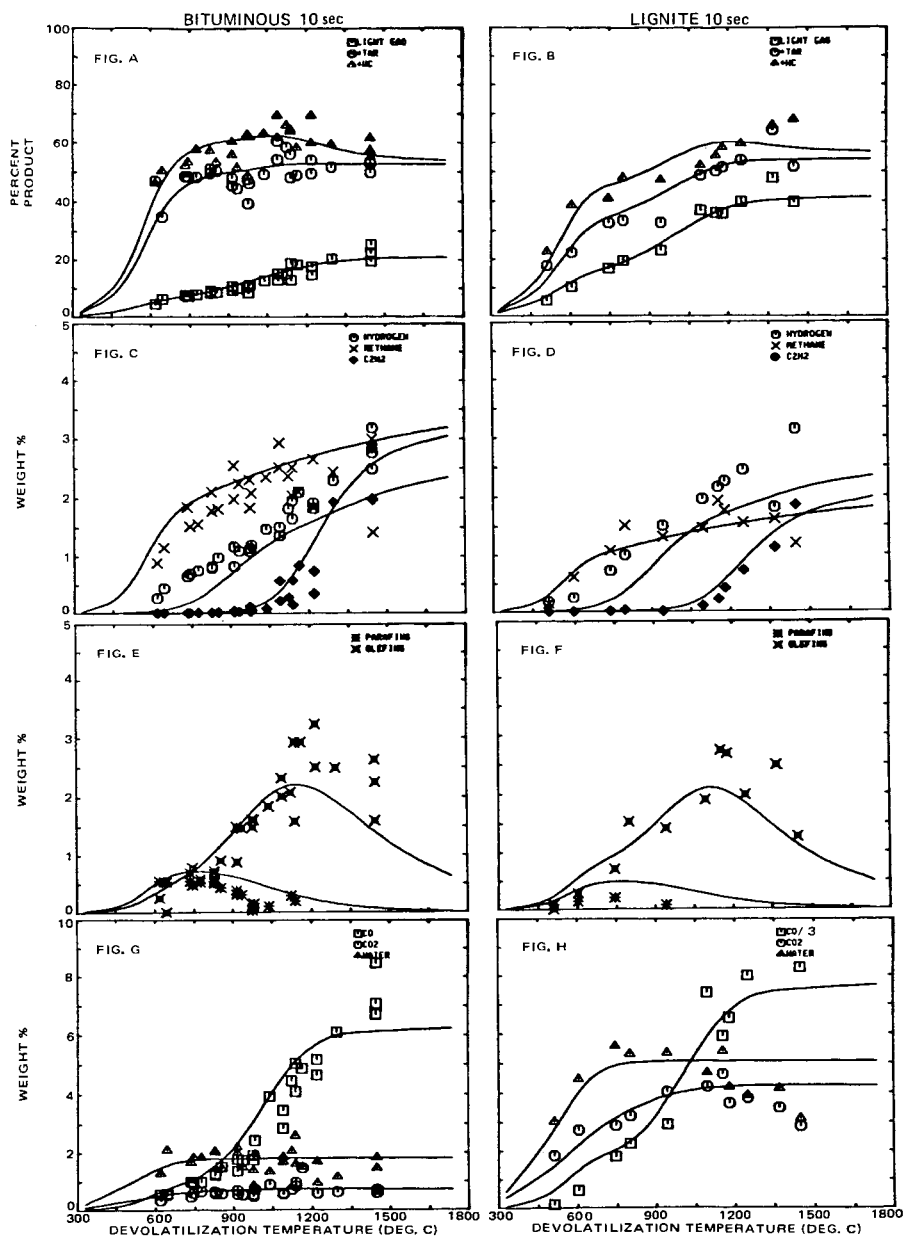


FIG. 5 PYROLYSIS PRODUCT YIELDS